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A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE BY AN IMPROVED STATIC METHOD.

DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy

by

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A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE BY AN IMPROVED STATIC METHOD.

The value of studying such a property of solutions as vapor pressure lies in the fact that it is a property which depends upon the number of parts of the dissolved substance. In such a respect it is entirely analogous to the boiling and freezing point of a solution and to its conductivity and osmotic pressure. The value of these properties in the determination of the molecular weight, and, in the case of electrolytes, of the dissociation, is too well-known to need amplification. That their value, however, is dependent on the accuracy with which they can be determined is also self-evident. The boiling-point method is really a dynamic method of measuring vapor pressure. The objection to both the boiling-point and freezing-point methods is that they are subject to appreciable correction factors for the constant errors. The enormous difficulty in measuring osmotic pressure makes it incapable of general application, while the conductivity method is least accurate in the region of high concentrations, where the constant errors in measuring vapor pressure are least.

In the past, the practical difficulties have prevented the accurate measurement of vapor pressure, because the lowerings produced by medium concentrations at ordinary temperatures are extremely small values (fractions of a millimeter), and are greatly affected by extraneous influences.

In the method evolved in this laboratory by Frazer and Lovelace[i], not only has the accuracy of measurement been greatly refined,(0.001 mm.), but the disturbing influences formerly regarded as irremovable, have been completely eliminated. The results published in this dissertation for aqueous solutions of mannite at 20°, are regarded as being the least open to criticism of any yet published, and are believed to differ by not more than 0.001 mm. from the true values. Before describing these results however, and the method by which they were obtained, it seems advisable to trace the evolution of methods used in the past to measure the property of vapor pressure.

These methods... are of two types, static and dynamic. The well-known boiling-point method is a dynamic method in which the pressure is kept constant and the elevation of the boiling-point noted. In all the static methods the pressure is allowed to vary and the temperature regulated. Aside from the constant sources of error in the boiling-point method, there is the added objection that the exact relation between changes in temperature and changes in pressure is unknown. A detailed discussion of the boiling-point method lies outside the scope of this paper. In presenting an outline of the other methods, it seems best to group the results obtained by their use together, rather than after a description of each apparatus.

I. THE STATIC METHOD.- In the static method the change in the vapor pressure of the solvent due to the dissolved substance is measured, the temperature being kept constant. The easiest way to follow the evolution of this method is to

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[i] J. Am. Chem. Soc. 36,2439(1914); Z. physik. Chem. 89, 155 (1914).

keep clearly in mind the constant sources of error. These are:

I. The presence of volatile impurities, especially dissolved gases like air, which themselves exert a vapor pressure.

2. Inaccurate bath regulation. Since vapor pressure is a function of temperature, this error is obvious.

3. Lack or inadequacy of a stirring device, resulting in surface concentration, with consequent change in vapor pressure.

4. The error due to the personal equation of the operator reading the difference in level of the mercury heights.

The significance of these errors will be made plain by a description of the earliest form of apparatus used. The first investigator to employ the static method for solutions on an extended scale was Wüllner.[i] The principle of his apparatus was exceedingly simple. The solution whose vapor pressure was to be determined was placed above the mercury in the vacuum of a barometer tube, and brought to the desired temperature by immersion in a regulated bath. The column of mercury is de--pressed, and by comparing its height with that of the mer--cury in a barometer tube containing the pure solvent, the lowering of the vapor pressure of the solvent due to the dissolved substance can be determined directly.

Wüllner's apparatus consisted of six tubes connected below by canals, and joined to a pump and to a manometer. He succeeded in regulating his bath to an accuracy of 0.I° by means of a stirrer subjected to about"three violent jerks" per

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[i] Pogg. Ann. I03, 529 (I858); I05,85(I858); II0, 387(I860)

minute. He estimates the magnitude of the constant errors as follows: I. To inadequate bath regulation, (especially at high temperatures) 2-to 4 mm.; to errors in reading the mercury levels, ±0.35mm.; to retained air, unknown, but presumably large. (The use of the water barometer was supposed to eliminate this error; but the amount of retained air is known to depend on the concentration of the solution.) Wüllner neglected entirely the error due to surface concentration . His method of removing air was to establish a partial vacuum and allow the air released to escape under mercury.

Tammann's[I] method was more accurate. The solution was placed in one limb of a U-tube which was nearly filled with mercury. The air was removed by boiling the liquid, and this limb was closed by the blow-pipe. The other limb was connected with a manometer and an air-pump, and the U-tube was immersed in a bath maintained at a constant temperature. The vapor pressure of the solution was found by reading the mercury level in both limbs and the manometer, after the pressure had been adjusted to a convenient amount. The vapor pressure of water was determined by simultaneous obsrevations made with a U-tube properly arranged with water in place of the salt solution. The only real difference between this method and that of Wüllner is in the means taken for removing air, the solutions being analysed subsequent to measurement rather than before. His estimated sources of error are somewhat smaller, however. He attributes o.I5mm. to dissolved air, ±0.I5 mm. to errors of reading, and ±2.00 mm. to variations in bath temperature. The percentage error is seldom more than 4% and usually I% or less, according to Tammann.

[I] Wied. Ann.24,523,(I885)

Pauchon[1] used the method of Regnault as applied by Magnus to solutions. Inasmuch, however, as the apparatus of Wüllner, already described, was modeled after that of Magnus, a description of this is unnecessary.

Emden[2] took particular pains to avoid all the constant errors. He considered the direct measurement of the vapor pressure of each salt solution to be necessary, whereas Wüllner, Tammann and Pauchon had measured this indirectly by comparing with the vapor pressure of water. Emden used an apparatus devised by Konowalow[3], for which he claimed that the solution could be obtained air-free in the apparatus without altering its concentration. A detailed description of this apparatus would lead too far. In principle, it involves the use of a high vacuum obtained by a mercury pump, for the purpose of removing air. Nevertheless, he was unable to remove air completely, because however high his vacuum, on standing a certain amount of air would rise from the solution, and on again admitting pres-sure this would redissolve. He found no means of overcoming this difficulty. The errors due to reading and to inaccurate bath control were somewhat lessened, but the main advance was in the method of removing air. Emden's apparatus represents the best development so far of the static method.

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1 Compt. rend. 89,I8,(I879)
2 Wied. Ann. 3I,I45,(I887)
3 Wied. Ann.I4,34(I88I)

Moser[1] used a static method which enabled him to measure the vapor pressure of solutions at low temper--tures. He substituted water for mercury as a means of measurement, but since his apparatus added no new feature with this exception, it is not necessary to describe it in detail.

Raoult[2] also used the static method. He claims an accuracy in the measurement of the absolute pressure of ether and of etheric solutions of 0.Imm. His method of removing dissolved gases is analogous to that of Tammann. He introduced a new feature, however, in stirring the solution. By alternately inclining and raising the apparatus, he could simultaneously stir all the solutions, and this was further facilitated by the presence of a plat--inum wire at the upper end of the tube. His bath regulation was accurate to $0.I^{o}$.

II. THE DYNAMIC METHOD.- The dynamic method superceded the static method because of supposedly greater accuracy, but the results obtained by its use have scarcely justified the claims made for it. In the dynamic method the vapor of a liquid is carried away by a current of air. Two types exist.

(A) The indirect dynamic method. This is based upon the principle that when air or some other inactive gas is saturated with the vapor of a liquid or solution, the

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[1] Wied. Ann. I4, 72,(I88I)

[2] Compt. rend. I03, II25(I886)
I04, 976, I430(I887)

following relation holds:

$$\frac{\text{total volume}}{\text{volume of aqueous vapor}} \qquad \frac{\text{total pressure}}{\text{pressure of aqueous vapor}}$$

Regnault[1] was the first to apply this principle, and his results agreed with those obtained by the static method.

In I888, Tammann[2] applied the same method. His values however, were in every case too low because of changes in surface concentration resulting from evaporation. Tammann thought to avoid this source of error by bubbling air through the solution, but this change introduced additional errors due to fluctuation in air pressure, and to the spattering of the solution by bubbles of air. Fluctuations in air pressure was another source of error, resulting in incomplete saturation of the air; and the drops of solution spattered on the walls of the vessel became concentrated by evaporation, so that the vapor pressure was reduced.

I n the above method five points are to be considered:

I. Exact measure of the volume of air.

2. Exact measure of the weight of water contained in that volume of air.

3. Exact measure of the barometric pressure.

4. Complete saturation of the air.

5. Exact measure of the temperature at which the air is saturated.

The chief sources of error are (I) inaccuracy in measuring the air, and (2) inadequate bath regulation.

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[1] Pogg. Ann. 93, 537 (1854)

[2] Wied. Ann. 35, 322 (1888)

It may be shown that a variation of 0.01° in the bath containing the solution, and of 0.1° in the aspirator containing the air, gives rise to an error of about 7% for a half-normal solution.

Kahlenberg[1] (and also Berkeley[2]) devised an improved saturator, which could be rocked back and forth so that a large and constantly fresh surface of liquid was exposed to the air. To insure complete saturation, the air was first supersaturated, and allowed to deposit its excess moisture before entering the saturator.

Lincoln and Klein[3] used the same method as did Kahlenberg.

Orndorff and Correll[4] aimed to simplify the dynamic method by dispensing with the thermostat. They did not get satisfactory results.

Carveth and Fowler[5] used U-tubes for saturators, and an air bath instead of a water thermostat.

Washburn[6] has recently undertaken to improve the dynamic method. Large saturators kept in constant motion are used to give complete saturation. His absorbers are of a special type, designed for readiness in weighing with

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1. Science, 22, 74 (1905)
2. Berkeley and Hartley Proc. Roy. Soc. A-77, 156 (1906)
3. Jour. Phys. Chem. Volume .....II, 318 (1907)
4. Jour. Phys. Chem. Vol. 1. p. 753 [1897]
5. " " " " 8, p. 313 [1904]
6. Jour. Am. Chem. Soc. 37, 309, (1915)

great accuracy. His method is to pass first through water, then through an absorber; then through the solution and another absorber; and finally through water again and through a third absorber. The theoretical accuracy of the method is about 0.25%: thus far the actual accuracy is 1-2%.

(B) The Differential Dynamic Method:- This method was first devised by Ostwald[1] and consisted simply in passing dry air through a solution, then through water, then through sulphuric acid. The loss of weight in the solution is proportional to its vapor pressure. The loss in weight of the water is proportional to the difference between the vapor pressure of the solvent and that of the solution. The gain in weight of the sulphuric acid should equal the sum of these losses and thus act as a check on the work. The relative lowering is thus found directly, since

$$\frac{\text{loss of weight in water}}{\text{total loss of weight of water + solution}} = \frac{p-p'}{p}$$

In this method the volume of air aspirated does not have to be known. To this extent the method of Ostwald is better than any preceding, but the other sources of error are still operative.

Will and Bredig[2] undertook to improve the method and to apply it to solutions in ether and alcohol. Instead of the three-bulb Liebig apparatus, they used flasks containing nine bulbs, thus increasing the opportunity for the air to

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1) Phys. Chem. Meas. p 188, (Walker's trans.)

2) B. 22, 1084, (1889).

become saturated.

Berkeley and Hartley[1] introduced the entirely new feature of agitating the saturator during the experiment.

RESULTS OBTAINED BY THE USE OF THE STATIC METHOD.

Regnault[3] and Magnus[2], the first to use the static method, worked principally with pure solvents, especially water, and arrived at no fundamental relation concerning solutions.

Von Babo[4] was the first to discover any relation between the vapor pressure of water and that of salt solutions. His experiments with calcium chloride and other salts led him to believe that the vapor pressure of a salt solution was at all temperatures proportional to that of pure water. He stated this in the form of an equation,

$$p = c\,P$$

where p is the vapor pressure of the salt solution, P that of pure water, and c is a constant. This law of von Babo constituted the bone of contention among subsequent workers for many years.

Wüllner was unable to confirm von Babo8s law. In fact, he pointed out that certain of the latter's own measurements were themselves not in accord with his generalization, and that his method led to appreciable errors. The principal contribution of Wüllner, however, was his enunciation of a general relation quite as important and fundamental as that

1,2,3,4, Loc. cit.

of von Babo concerning the effect of temperature. This was to define the effect of different concentrations on the vapor pressure. Wüllner announced that " The lowering of the vapor pressure of water due to a dissolved substance, was always proportional to the concentration of the substance in solution."

The correctness of this generalization was disputed by later workers. The problem was complicated by two factors:
1.The use of absolute instead of equivalent weights.
2.Failure to recognize the phenomena of dissociation.
At this time the theory of electrolytic dissociation was of course unknown. In fact, it is difficult to see how Wüllner could arrive at such a generalization except by the use of salts with nearly equal molecular weights, and similar dissociation constants. As a matter of fact, Wüllner labored under exactly this difficulty in finding deviations in both directions from von Babo's law, but it does not seem to have affected his own.

Pauchon, however, found the same difficulty with the law of Wüllner that the latter had found with the law of von Babo. He found that the change in the lowering produced by changes in concentration followed a more complex law, where constants for the concentration were introduced as correction factors. This is exactly what we should expect for aqueous solutions of electrolytes.

Tammann foreshadowed the results of Raoult by discovering that chemically similar salts produce nearly the same molecular diminution of vapor pressure. It is to be noted that his statement reads "chemically similar", which in this case means ionization constants of nearly the same value. A perusal of his table brings out the fact that the best con-

-stants were obtained for the alkali salts of strong mineral acids. His use of equivalent weights eliminated the second difficulty. He, also, was unable to confirm von Babo's law.

As a general criticism of the results of Wüllner, Tam--mann and Pauchon, and incidentally of their method of work, Emden[1] pointed out that while none of these workers had confirmed the law of von Babo, they were equally unanimous in disagreeing among themselves. While, for instance, Wüll--ner and Tammann found deviations from the law in both direct--ions, for the same salt they would frequently disagree as to the direction of the deviation. And where these workers had agreed in finding deviations in both directions, Pauchon had found them in only one direction.

Emden was consequently led to repeat their experiments with an improved method . As a result of his work, he found that von Babo's law held between the temperatures 20° and 95°. It will be impossible to give his method of calculating his results, owing to lack of space. He used an interpolation formula suggested by Magnus, applicable both to water and to the solution. Emden failed to confirm the law of Wüllner.

Moser, as already stated, devised a method applicable at low temperatures. He confirmed the results of Wüllner but added nothing new.

Raoult reached the most important generalizations con-cerning vapor pressure. His name is especially associated

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1. Loc. cit.

with the law which states that equivalent weights of dif--ferent substances produce an equal lowering of the vapor pressure, when dissolved in the same amount of solvent.I.E, the lowerings of vapor pressure of different solvents are equal when the ratio of the number of molecules of the dissolved substance to the number of molecules of the sol--vent is the same. It should be remembered,however, that the equations of Raoult hold only for dilute aqueous solu--tions of non-electrolytes, and for organic solvents. In fact, it was by avoiding aqueous solutions entirely that he arrived at his generalization. Raoult worked entirely with organic solvents, and by so doing was able to confirm both Wullner's law, and that of von Babo concerning the effect of temperature, and also to reach the important generalization already stated. It is especially interest--ing to note that these important results were obtained by the use of a static method.

RESULTS OBTAINED BY THE DYNAMIC METHOD.

In actual results the dynamic method has proved less fruitful than the static method,by which the classical researches of Raoult were accomplished.

The first results thus obtained were those of Regnault. They agreed with those obtained earlier by the use of the static method.

Tammann's results were too low, due to the errors already mentioned. These results were probably less accurate than the theoretical deviation calls for (7° for a 0.5 N. solution.)

Ostwald and Walker, by the indirect dynamic method, obtained much better results than did Regnault and Tammann.

Will and Bredig worked with organic solvents and approximated an accuracy of about 8 %.

Berkeley and Hartley obtained results which were un--doubtedly too low. They usod the method for determining the osmotic pressure of aqueous solutions of $Ca_2Fe(CN)_6$, and of cane sugar. Their accuracy does not exceed 5%.

Kahlenberg has published but little data; but that which has been published shows large variations in measure--ments on individual concentrations. The conclusions arrived at in several instances are very interesting. Krauskopf,who worked with Kahlenberg, found that for KCl and NaCl the molecular weight increases with dilution. This is just the opposite of what one would expect from the theory of electrolytic dissociation. For cane sugar, Krauskopf found that the molecular weight decreases with dilution.

Lincoln and Klein, using the same method , found that for KNO_3 , the molecular weights are in accord with the electrolytic theory. $NaNO_3$ and $LiNO_3$,however, are at variance with this theory, since the molecular weight of lithium nitrate is less than that calculated on the basis of complete dissociation. They conclude that the lowering of vapor pressure is not solely a function of the number of parts of the dissolved substance in solution, but that th the individuality of the particular salt manifests itself, and must be taken into consideration.

The results of Carveth and Fowler were of such a

character as to lead them to doubt the accuracy of any results obtained by the air-bubbling method.

Perman obtained very accurate results, but deviations of from 5 to 15% sometimes occur. His second paper deals with a hydrate theory advanced by Callender[1], who maintains that there may exist in solution a few definite chemical hydrates. This is apparently the same as Mendelejeff's hydrate theory. Perman interprets his results in a way which disproves this, and confirms the hydrate theory as advanced by Jones[2].

Washburn's results have already been mentioned as showing an actual accuracy of 1-2% and a theoretical accur--acy of 0.25%.

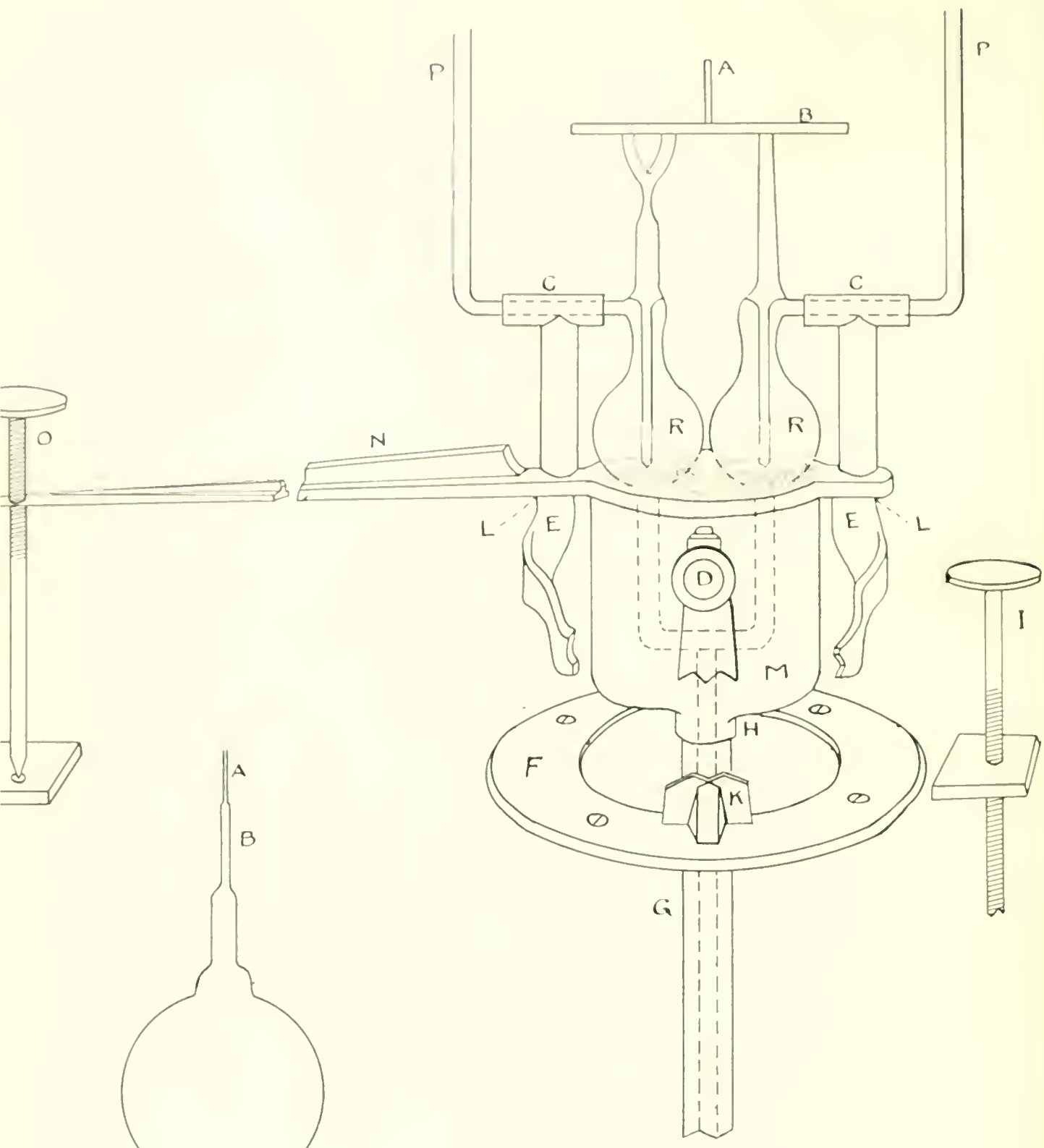

Fig. 5a

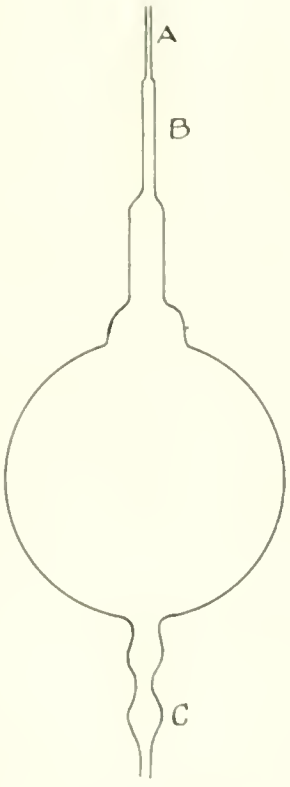

Fig. 4a

THE METHOD OF FRAZER AND LOVELACE.[1]

As already stated, there are four difficulties involved in the use of the static method. These are:

1. The measurement of small differences in vapor pressure.

2. The necessity for the complete removal of air.

3. The necessity for accurate bath regulation.

4. The necessity of stirring the solution.

The solution of all these points means the perfection of the static method.

Since the whole apparatus is built around the Rayleigh manometer[2], used to overcome the [illegible] difficulty of actual measurement, this will be described first. This instrument, designed by Lord Rayleigh, was used by him to measure small differences in gas pressure. In the apparatus of Frazer and Lovelace, it is used to measure the difference between the vapor pressure of the solution and that of the pure solvent.

The principle of the manometer is best understood by a description of its parts. (See Fig 5a) R R are glass bulbs, about 39mm. in diameter, blown on a glass fork. The lower end of this fork is connected by means of a rubber tube with a mercury reservoir which may be adjusted very accurately to any

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1. Loc. Cit.

2. Z. physik. Chem. 37, 713, (1901)
   Trans. Royal Soc. 196. 205, (1901)

desired height by means of the screw I. Extending to the centre of each bulb is a glass rod( ), ground at the end to a very fine point, for accuracy in adjusting. The side--limbs P,P' communicate with the systems, the relative vapor pressures in which are to be measured. Thecbulbs are set in plaster in an iron pot, M , which is mounted on a hori--zontal axis, D , at right angles to the vertical plane passing through the points. The bulbs can be rotated on the axis D by means of the screw O.

To measure small differences in pressure we proceed as follows: First, the same pressure is maintained in both bulbs, either by evacuating them to the limit of the pump, or, after complete removal of air(in a manner to be described later) , subjecting them to the same pressure of aqueous vapor. Either the solvent or the solution may be used for this purpose. By rotating the bulbs and raising the mercury level, the glass points may be brought into exact coincidence with their images in the mercury. This is facilitated by the use of microscopes magnifying about six diameters. This position of the points is called the " zero " position.

Now decrease the pressure in one limb of the manometer by introducing into that limb the vapor of the solution. The mercury in the bulb connected with this limb will of course rise, and the degree of rotation necessary to restore coincidence of the points will be a measure of the lowering of vapor pressure. Also the distance between the points is a factor. Obviously, we could measure this rotation by knowing the pitch of the screw, and the angle through which it turns. A more accurate method is by means of a cath--etometer, the principle of which is well-known. A mirror

is placed at A in a plane parallel to the axis of rotation. By means of a telescope placed about three meters away, any change in the position of this mirror produces a correspondingly large change in the reading on a scale placed besid e the telescope, the magnitude of the ch nge being proportional to the distance of the mirror from the scale.

To determine the change in actual vapor pressure from the scale deflection, we must, then, know

1) the distance between the points, d.

2) the distance from mirror to scale, D.

3) the scale deflection, s.

Then if h is the difference in pressure in the two limbs of the manometer corresponding to an angle of rotation θ, we have:-

$$h = d\sin\theta \qquad \text{and} \qquad s = D\tan\theta$$

and,

$$h = \frac{ds}{2D}\,\frac{\sin\theta}{1/2\tan 2\theta}$$

Now, for all values of θ up to 1^o, $\frac{\sin\theta}{1/2\tan 2\theta}$ may be regarded as unity, and our formula becomes,

$$h = ds/2D$$

Since for the particular instrument used the value 1^o for θ corresponds approximately to the depression of a three-molar solution of a non-electrolyte, and since the concentrations measured never exceed this value, it follows that we may use the simpler formula, The other values for the instrument are

$$d = 38.88 \quad \text{and} \quad D = 3334.6$$

$$\text{Hence, } s = \frac{2 \,/\, 3334.6 \,/\, 1}{38.88} = 171.53$$

This value, 171.53, represents the deflection of the scale corresponding to 1 mm. actual depression in vapor pressure.

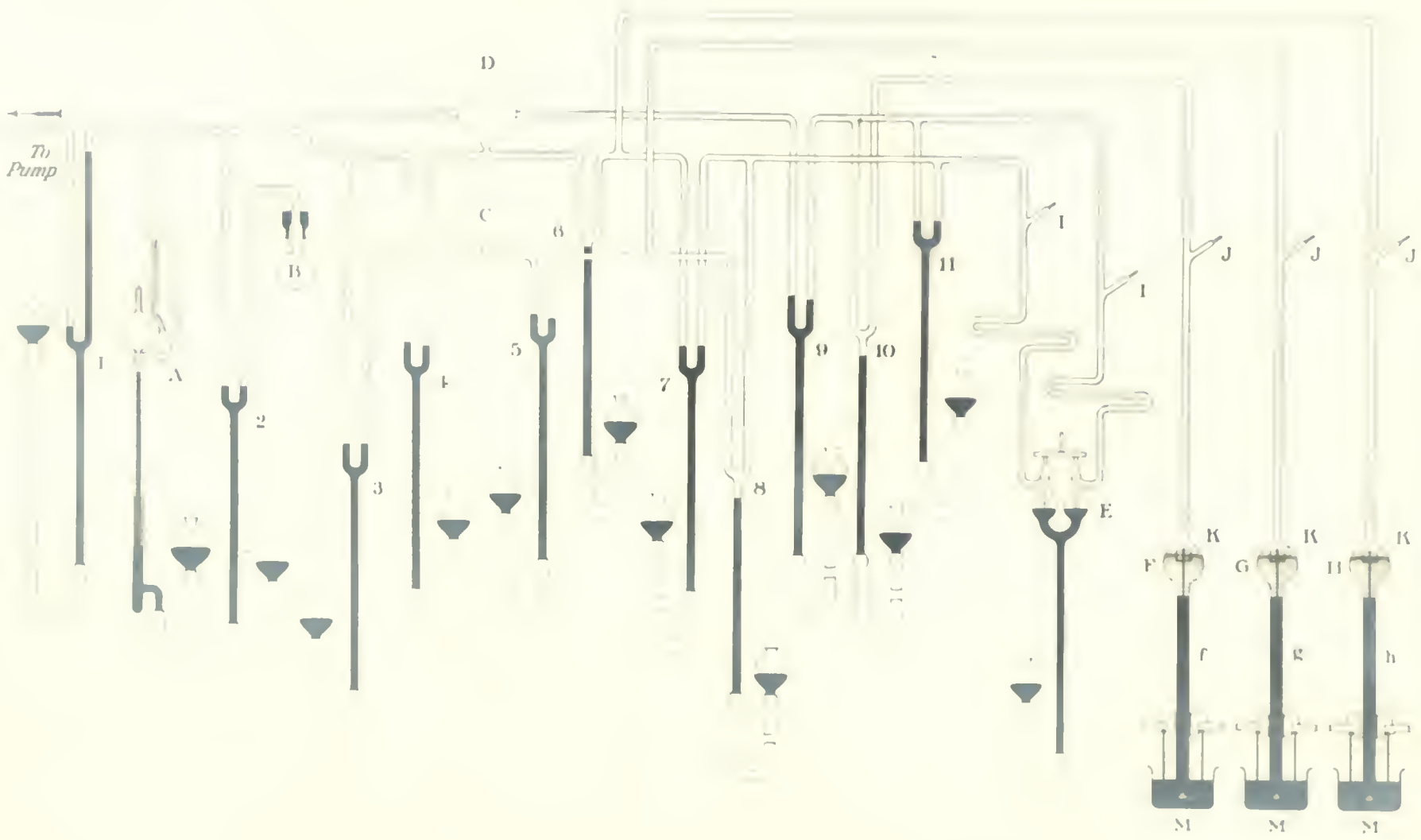


Figure II

Therefore, 1 mm. on the scale = .00583mm. difference in pressure, in the two bulbs. By observing the points through microscopes of 25 mm. focus, mounted on the instrument and rotating with it, the operator can set the points to an accuracy of 0.1 mm. on the scale, which corresponds to a difference in pressure of 0.000583 mm. This represents the theoretical limit of accuracy of the method, and is approximately that claimed by Rayleigh for his manometer, of which the one used in this work is practically a reproduction. An instrument of this kind represents an enormous advance over all previous methods used in the static method for measuring the difference in the height of the mercury levels. For example, the greatest accuracy in reading claimed by any previous investigator in measuring vapor pressure by the static method was ±.15mm.; so that this instrument would then be 250 times more accurate than the older methods.

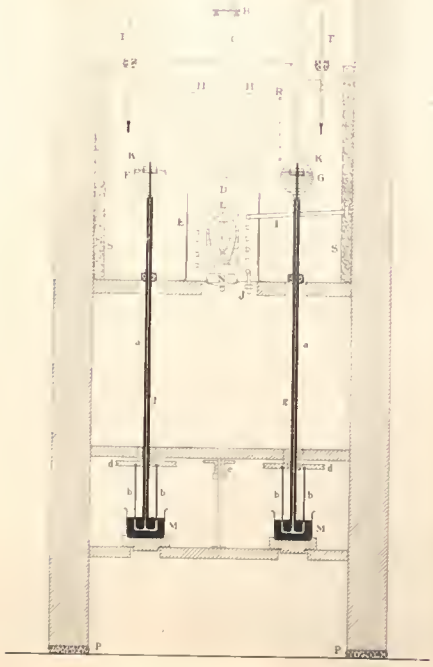
The second great difficulty in the static method is the complete removal of air from both solution and solvent. This is brought about by means of a series of mercury traps which act as stop-cocks (see Figure II). These traps open or close the entrance to large bulbs, (C and D), into which the vapor of the solution or solvent can be expanded. After expansion, the given trap is closed, the water vapor absorbed in the pentoxide bulb B, and the air removed by means of the pump. This process is repeated again and again, until the McLeod gauge (A) shows a pressure of air less than 0.0004 mm.

As shown in the figure, the entire apparatus is built around the Rayleigh manometer(E). One side of the manometer

communicates with the solvent bulb, F ,and the other with the solution bulbs, G and H. 1,2,3,4,5,6,7,8,9,10,11 are the mercury traps already referred to. They may be opened or closed by adjusting the position of the mercury reservoirs. The long traps are a little more than barometric height, while the short ones are about 100 mm. high. By using mercury traps for stopcocks, leaks in the apparatus are rendered impossible. The phosphorous pentoxide bulb (B), is provided with a ground glass joint and a mercury seal. (A) is the McLeod gauge, capable of showing a difference of pressure of 0.0004 mm. All connecting tubes are seven mm. internal diameter. I,I and J ,J ,J are projecting tubes used in cleaning the apparatus. The bends in the two limbs of the Rayleigh manometer are for the purpose of giving greater flexibility in rotating the instrument. It will be observed that with such a system of traps and bulbs, it is possible to measure the depression of one solution, while another is being expanded for the purpose of removing air, This is exactly illustrated in Figure II, in which the mercury traps are adjusted to measure the depression of the solution in bulb G, and also adjusted to expand the solution in bulb H .

The third necessity in measuring the vapor pressure of solutions is accurate bath regulation. A sketch of the bath is given in Figure III, and of the thermoregulator in Figure IV. The solvent bulb ,(F) and the solution bulb (G) ,as shown in the cross-section, are fixed about mid-way in the bath. The water is stirred by a propellor revolving at the rate of about 575 revolutions per minute. The swirling motion is counteracted by

FIGURE III.



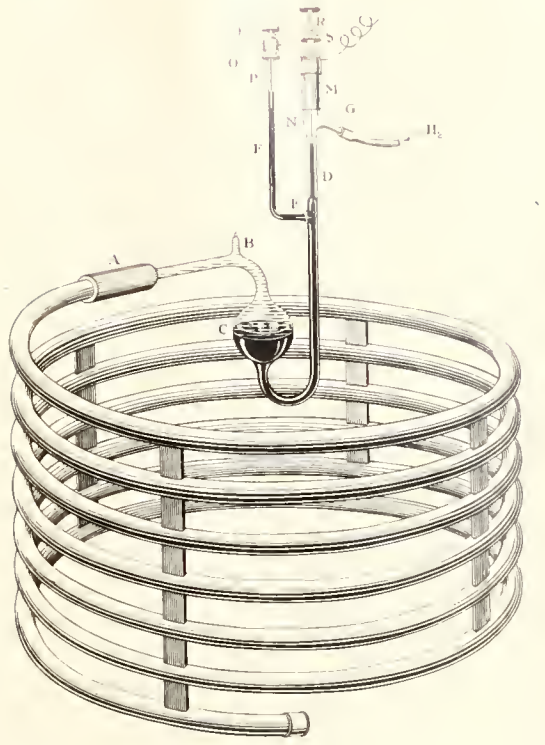
by the flanges H , H, and the propellor is of such a shape as to throw the water upward in revolving, thus insuring an even distribution of the water over the heating surface, L, and over the cooling coils, I. The bulbs are so placed in the bath that they are at identical distances from both the heating and cooling surfaces;so that any inequalities of bath temperature which might exist, would affect all alike. However, the records of temperature regulation would seem to indicate that such inequalities do not exist. The bath is made of copper, and is insulated with felt,(S.)

Specimen Record of Bath Regulation.

The following records of bath regulation, taken from the laboratory note-book, will serve to illustrate the great constancy of regulation during the time necessary for a complete experiment (which is always less than one day.) The readings were taken on a Beckmann thermometer.

November 8, 1914.	9.00 A.M.	1.6580°
	10.45 "	1.6575
	1.00 "	1.6575
	2.00 "	1.6575
	3.00 "	1.6575
	7.30 "-	1.6575
November 11. 1914.	9.45 A.M.	1.662
	10.30 "	1.662
	12.30 P.M.	1.660
	4.00 "	1.662
	5.10 "	1.662
	7.30 "	1.662
	9.15 "	1.662
November 24, 1915.	11.25 A.M.	1.6585
	2.45 P.M.	1.6585
	4.30 "	1.6585
	4.55 "	1.6585
	8.00 "	1.6585

FIGURE IV.



The thermoregulator is shown in Figure IV, above. This is a toluene-mercury instrument, and is capable of regulating the temperature of the bath to 0.001° for days at a time without variation. The principle of such a regulator is well-known. M is a platinum (or tungsten) point through which electrical contact is made with the mercury in the narrow tube D, when the temperature of the instrument rises above a certain point, (fixed in this case at about 20° by adjusting the screw R.) M is a metal sheath which is fixed firmly in position by means of sealing-wax, and which can be removed for the purpose of clean-

ing the mercury in D. A platinum wire, sealed in the wall of the glass tube at F, completes the necessary circuit between the mercury subject to expansion, and the mercury in the tube E ; which is used only to make contact. A steady stream of hydrogen is kept passing through the tube G, in order to prevent the oxidation of the surface of the mercury in D. This has been found to lengthen the time during which the regulator will act as desired; but the surface of the mercury in D will gradually become less bright in appearance, and must be replaced by fresh metal (usually about every ten days or two weeks.) The bulb is filled with mercury to the level C, and the rest of the apparatus including the coils, with toluene. The projecting tube B is used in filling the instrument. The glass tube is joined to the copper coil at A. The glass is sealed to a platinum disc, which is in turn sealed to the upper copper coil by means of brass.

The great sensitiveness of this thermoregulator is due to the high coefficient of expansion of toluene, The copper used for the coils has a somewhat greater coefficient of expansion than glass, but, on the other hand, its conductivity for heat is much greater than that of glass, so that it is preferable to the latter, and has the additional advantage of being less fragile.

4. The necessity of stirring the solution. As already stated this constitutes the fourth great problem in connection with the static method. The device employed in the apparatus of Frazer and Lovelace, for the purpose of overcoming this difficulty, is perhaps the most ingenious feature of the whole apparatus, (see Fig. III), a, a are glass rods of 5 mm. diameter, extending up into the solution and solvent, and bearing at their upper end a platinum disc, I

to facilitate stirring. At their lower ends (L,L), two glass rods are fused into a T-arrangement, whose upper ends are fixed in the wooden pulleys (d,d). By connecting these pulleys with one in the centre, in turn joined to a motor, the rods bearing the platinum discs are automatically turned, and thus both solution and solvent are stirred at the same rate. There is no friction of the T-joint against the bottom of the cup, since the rod, being of less density than the mercury, is held in place by the vacuum above. Experiments indicate that the rate of stirring has no influence on the deflection.

In carrying out a complete experiment we proceed as follows: Sufficient mercury is poured into each cup, so that when a vacuum is established in the bulbs and in the rest of the system, there will be enough to form a column of barometric height, and a little more, to close the end of the tube. When this vacuum is established, the solvent and the solution, partially freed from air by a method to be described later, are introduced into thier respective bulbs. Air is next completely removed from both solution and solvent in the manner already described, after which the zero point may be redetermined. The traps are then so adjusted that the vapor of the solvent is on one side of the manometer, and that of the solution on the other side. The two pressures are balanced against each other and the scale deflection is read. The difference between the value obtained for the zero and that for the solution represents the lowering as expressed in scale divisions. By the relation already deduced , one mm. of the scale equals .000583 mm. actual vapor pressure. Hence, [ ] the scale deflection, multiplied

by .000383, gives the lowering of the vapor pressure of the pure solvent by the amount of dissolved substance present. A description of the preliminary treatment to remove air, and a more detailed discussion of the manipulation follows:

The Solvent. Inasmuch as the preliminary treatment of the solvent to remove air is much like that used for the solution, this will serve to illustrate both. A bulb (Fig. 4a is used into which the solvent can be readily introduced at the bottom(C). The upper tube is later drawn out to a very fine capillary, (A) (about 0.05 mm.), or so fine ,that the amount lost by the vaporization of the solvent is negligible. The solvent is first partially freed from air by boiling, and next introduced into the bulb. The lower end of the bulb is then sealed with the blow-pipe, and the bulb containing the solvent is heated to about 90°, or to such a point where the expanded solution just fills the small capillary. The latter is then sealed, and the bulb and solvent cooled gradually to room-temperature. A partial vacuum is thus established, into which most of the residual air present in the liquid will escape. By repeating the process about five times, the greater part of this residual air can be removed,before introducing the solvent into the apparatus. This shortens considerably the proceedure of removing air after introduction. Experiments indicate, that when a capillary of proper size is used, the loss through vaporization of the solvent is altogether a negligible quantity. E.G. A bulb containing over three hundred grams of water lost only two and one-half milligrams, after heating for six hours at a temperature of 90°. Due correction

of course was made for the loss in weight of the glass by solution in the bath employed, by heating a partially evacuated bulb, weighted with mercury, and sealed at the capillary.

The Solution. Although the point just discussed is of no importance in the case of the pure solvent, it is vital in the preparation of the solution, where the effort to measure exact normalities, necessitates introducing a solution of known concentration. In so doing, allowance must be made for the concentration of the solution subsequently to removing air, a process to be described immediately.

The solutions are so made up that 0.1 % loss in weight of water will render them of the exact normality desired. The weight normal system is used, that is , by a normal solution is meant one in which a gram molecular weight of the substance is dissolved in 1000 grams of water. Analysis subsequent to measurement indicates that the increase in the concentration of the solution ....., due to loss of water is never more than 0.1 %; and further, that for a normal number of exhaustions, as described later, this increase is about 0.06 to 0.08 %. That is, the solutions were about 0.03 % less than the normality desired. Since the accuracy of the method, even for the most concentrated solutions, is about 0.1% , it follows that this degree of divergence from the actual normality is entirely negligible. It is interesting to note that the calculation of the loss of water by evaporation into a known volume of the system, checks the value determined experimentally as above.

In introducing either solution or solvent into the system the same procedure is adopted. This is as follows: A mercury reservoir is joined to the lower end of the sealed bulb containing for example the solution. The small capillary is joined to a rubber at whose lower end is a hooked tube of small internal bore, which can be placed beneath the lower end of the tube leading to the solution (see Figure III, at the point M.) Both ends of the bulb are opened by breaking the glass tubes, and after a small amount of solution has been allowed to escape, the hooked tube is placed under the solution bulb, and the solution allowed to flow up the tube, by regulating the flow from the mercury reservoir. The solvent is introduced in an exactly similar manner. The bulbs in the bath are filled about two-thirds full, or so that the platinum stirring device is from one-quarter to one-half an inch out of the solution.

When both solution and solvent have been introduced, the next problem is to remove the last trace of dissolved air. This constitutes the major part of the whole operation, and is often very time-consuming. Reference to Figure II , which illustrates the series of traps, will make this operation clear. To remove air from the solution, we would proceed as follows:-

Traps 6 and 7 are closed, and a vacuum exists in the bulb D . Then trap 4 is closed , and trap 6 is opened; this admits the vapor of the solution to the bulb D. The sudden vaporization of the solvent carries considerable dissolved air into the bulb, and this is further facilitated by stirring the

solution for several hours after expansion. When a sufficient length of time has elapsed for equilibrium to become established, trap 6 is closed and trap 4 is opened. Trap 2, leading to the pentoxide bulb, is opened to absorb the water vapor in the bulb, and the air is then removed by means of the pump, (by opening trap 1)If the amount of air is to be determined, then, after the absorption of the water vapor as above, the McLeod gauge is opened (trap at A), and the pressure determined.

Observations on the Rayleigh manometer during the process of removing air, show that as long as any air remains in the solution, even the smallest trace, a very long time is necessary for the establishment of equilibrium, when balancing the vapor of the solution against that of the air-free solvent. The pressure in the solution limb of the manometer, at first very nearly the true vapor pressure of the solution, slowly increases for 24 or 48 hours, depending on how much air remains. After equilibrium is attained, the difference in pressure in the two limbs is read in the usual way by noting the scale deflection. To this apparent depression, is added the air pressure in the system, subsequently determined by means of the McLeod gauge, after absorption of the water by the phosphorous pentoxide. The depression thus obtained agrees very closely, to about 0.001 mm. with the true depression measured later, after complete removal of air. When the solution becomes air-free, equilibrium is always reached in from 15 to 20 minutes.

When the apparatus was being built, the McLeod gauge was included in the system for the purpose of showing when

the removal of air was complete. As a matter of fact, however, the gauge is not necessary for this purpose. Given an air-free solvent in one bulb, the operator can follow very closely the progress of removal of air from the solution in the other bulb by observations on the Rayleigh manometer, and can tell with great accuracy, without the use of the McLeod gauge, when the removal of air is complete.

While it has been found necessary to regulate very accurately the temperature of the solution and solvent in the bath, no such constancy is necessary for other parts of the system, although the room temperature is kept fairly constant, about 24°- 26°, several degrees above that of the bath. This is because, when all air has been eliminated, equilibrium between solution and vapor is very quickly established, so that slight changes of room temperature, unless they are too sudden, merely cause evaporation or condensation of slight amounts of water, without affecting pressure. The only possibility of error would be the case where the temperature of one limb varied during a single experiment, without equal variation of the other limb, and where the readings were taken before the new equilibrium had a chance to become established. Inasmuch, however, as any given series of deflection readings usually extends over a period of an hour or more, and as the heating conditions in the room are maintained at approximately the same temperature, this possibility of error is greatly minimized. This appears to be the only feature about the apparatus which could be improved, especially in the manner of illuminating the mercury surfaces of the manometer in such a way as to prevent heat radiation from the source of the light.

EXPERIMENTAL.

In the following tables, the results with five experiments with aqueous solutions of mannite are given. As already stated, the solutions are made up on a weight normal basis, due allowance being made for the known amount of solvent that is to be lost during subsequent removal of dissolved air.

Experiment 1. 0.1-molar Mannite.

The solution was introduced Jan. 27, 1915. By Feb. 12, the air was completely removed. Final readings were taken as follows:

Feb. 12. Zero.

2.47 P.M.	8.65
2.53 "	8.65
2.57 "	8.70
Mean	8.68

Reading

4.10 P.M.	14.00
4.17 "	13.90
4.20 "	13.90
Mean	13.93

Deflection 5.25

Feb. 14. Zero.

9.03 P.M.	8.15
9.07 "	8.25
9.10 "	8.15
Mean	8.18

Reading

9.40 P.M.	13.45
9.45 "	13.40
9.50 "	13.45
Mean	13.42

Deflection 5.24

Feb. 15. Zero.

12.20 P.M.		7.90
12.25 "		8.00
12.35 "		7.90
	Mean	7.93

Reading.

1.40 P.M.		13.00
1.45 "		13.05
1.50 "		12.95
	Mean	13.00
	Deflection	5.07

Feb. 16.Zero.

12.13 P.M.		7.05
12.19 "		7.00
12.23 "		7.00
	Mean	7.02

Reading.

12.45 P.M.		11.70
12.50 "		12.00
12.53 "		11.85
1.00 "		12.00
	Mean	11.89
	Deflection	4.87

Feb.17 . Zero.

1.20 P.M.		7.30
1.25 "		7.30
1.20 "		7.20
	Mean	7.27

Reading.

12.45 P.M.		11.80
12.52 "		12.00
12.54 "		12.00
	Mean	11.87
	Deflection	4.60

Feb. 19. Zero.

11.57 A.M.		7.85
12.03 P.M.		7.80
12.10 "		7.85
	Mean	7.83

Reading.

3.18 P.M.		12.05
3.27 "		12.05
3.31 "		12.10
	Mean	12.07
	Deflection	4.24

Feb. 23, Zero.

12.03 P.M.		6.80
12.07 "		6.75
12.11 "		6.70
	Mean	6.75

Reading.

4.25P.M.		11.15
4.35 "		11.25
4.40 "		11.10
	Mean	11.20
	Deflection	4.45

Feb. 24. Zero.

12.01 P.M.		6.35
12.05 "		6.30
12.10 "		6.30
	Mean	6.32

Reading.

11.23 A.M.		11.95
11.25 "		12.00
11.30 "		12.00
	Mean	11.98
	Deflection	4.90

Zero.

12.29 P.M.		7.10
12.32 P.M.		7.20
12.42 "		7.00
12.50 "		7.00
	Mean	7.08

0.1-molar Mannite (continued)

Feb. 24,(continued)

Zero.

4.20 P.M.	7.10
4.26 "	7.15
4.55 "	7.20
Mean	7.18

Reading.

3.07 P.M.	11.95
3.13 "	12.00
3.54 "	12.00
Mean	11.98

Deflection 4.80

Feb. 25. Zero.

12.42 P.M.	6.00
12.54 "	6.15
12.56 "	6.00
12.58 "	6.15
Mean	6.06

Reading.

11.50 A.M.	11.15
12.07 P.M.	11.20
12.12 "	11.20
Mean	11.18

Deflection 5.12

Zero.

2.45 P.M.	6.65
2.48 "	6.90
2.58 "	6.70
3.04 "	6.75
Mean	6.75

Reading.

3.56 P.M.	11.40
4.03 "	11.30
4.10 "	11.40
Mean	11.38

Deflection 5.36

Feb. 25 (continued) Zero.

3.09 P.M.		6.05
5.13 "		6.00
	Mean	6.02

Reading.

4.16 P.M.		10.75
4.18 "		10.70
4.34 "		10.50
	Mean	10.65
	Deflection	4.63

Zero.

9.33 P.M.		7.05
9.45 "		6.95
9.54 "		7.00
	Mean	7.00

Reading.

8.09 P.M.		12.00
8.17 "		12.00
8.26 "		12.10
	Mean	12.03

Feb. 26. Zero.

4.45 P.M.		6.10
4.50 "		6.05
5.08 "		6.00
	Mean	6.05

Reading.

3.50 P.M.		11.00
4.00 "		11.00
4.06 "		11.00
	Mean	11.00
	Deflection	4.95

Feb. 27. Zero.

11.55 P.M.		6.60
12.02 A.M.		6.60
12.10 "		6.60
	Mean	6.60

Reading.

2.15 P.M.		11.50
2.20 "		11.60
2.25 "		11.50
2.30 "		11.60
	Mean	11.55
	Deflection	4.95

Mean of all readings, 4,90 . Depression, 0.0286 mm.

T = 30°.08+

Experiment 2. 0.2 molar Mannite.

The solution was introduced Dec. 15, 1915, and found to be air-free, Jan. 1, 1915.

Final readings were taken as follows:

		Zero		Reading	Deflection
Jan. 1, 1915.		8.80			
		8.70		17.75	
		8.60		17.80	
		8.65		17.75	
		8.70		———	
	Mean	8.69	Mean	17.77	9.08
		8.00			
		8.20			
		8.00		17.00	
		8.00		17.20	
		8.10		17.10	
	Mean	8.10	Mean	17.10	9.00
Jan. 23rd,		8.95		18.05	
		9.00		18.00	
		9.00		18.10	
	Mean	8.98	Mean	18.05	9.07
		8.15		17.75	
		8.10		17.75	
		8.15		17.75	
	Mean	8.13	Mean	17.75	9.62

0.2 molar Mannite (continued)

Jan. 25th,	Zero		Reading	Deflection
	9.10		18.75	
	9.00		18.80	
	9.15		18.80	
Mean	9.08	Mean	18.78	9.70
Jan. 26th,	9.00		18.90	
	9.00		19.00	
	9.00		19.00	
Mean	9.00	Mean	18.96	9.96
	9.10			
	9.20		19.30	
	9.20		19.15	
Mean	9.17	Mean	19.22	10.05
Jan. 27th,	8.95		19.20	
	9.00		19.10	
	9.10		19,10	
Mean	9.02	Mean	19.13	10.02
Jan. 29th,			18.00	
	8.15		18.05	
	8.05		18.25	
	8.00		18.05	
Mean	8.07	Mean	18.09	10.02
Feb. 1st,	8.70		19.05	
	8.75		18.95	
	8.80		18.80	
Mean	8.75	Mean	18.93	10.18

0.2 molar Mannite (continued)

		Zero		Reading	Reflection
Feb. 1st,		9.10			
		9.20		19.40	
		9.35		19.20	
		9.25		19.25	
	Mean	9.22	Mean	19.28	10.06
Feb. 3rd.		8.85			
		8.85		19.15	
		8.80		19.00	
		8.90		19.15	
	Mean	8.85	Mean	19.10	10.25
		7.80		18.00	
		7.90		18.05	
		7.80		18.15	
	Mean	7.87	Mean	18.07	10.20
Feb. 6th.		9.05		19.20	
		9.10		19.35	
		9.15		19.20	
		9.05		19.20	
	Mean	9.08	Mean	19.25	10.17
		8.20		18.30	
		7.95		18.10	
		7.85		18.20	
		8.00		18.25	
	Mean	8.00	Mean	18.21	10.21

0.2 molar Mannite (continued)

	Zero		Reading	Deflection
Feb. 9th	8.65		18.80	
	8.60		18.85	
	8.70		18.85	
	Mean 8.65	Mean	18.84	10.19
Feb. 11th,	7.90		17.65	
	7.90		17.70	
	8.00		17.70	
	Mean 7.93	Mean	17.68	9.75
			17.90	
			18.00	
			17.85	
		Mean	17.93	10.19
	8.70		18.70	
	8.70		18.70	
	Mean 8.70	Mean	18.70	10.00
Feb. 13th,	8.65		19.15	
	8.65		19.10	
	8.70		19.15	
	Mean 8.67	Mean	19.13	10.46
Feb. 15th,	7.00		17.60	
	7.10		17.60	
	7.10		17.50	
	Mean 7.07	Mean	17.58	10.51

0.2 molar Mannite (continued)

Feb. 15th,	Zero		Reading	Deflection
	8.15		18.20	
	8.25		18.10	
	8.15		18.15	
Mean	8.18	Mean	18.18	10.00
Feb. 16th,	7.00		16.35	
	7.05		16.20	
	7.00		16.25	
	7.00		16.30	
Mean	7.02	Mean	16.28	9.26
			17.90	
			17.90	
			17.80	
	7.95		18.00	
	8.00		18.00	
	8.00		17.80	
Mean	7.98	Mean	17.90	9.92
Feb. 17th.			17.10	
	7.30		17.30	
	7.20		17.15	
	7.30		17.05	
Mean	7.38	Mean	17.15	9.87
Feb. 19th.	7.25			
	7.10			
	7.30		17.25	
	7.30		17.35	
Mean	7.24	Mean	17.25	10.01

0.2 molar Mannite (continued)

Feb. 19th.	Zero		Reading	Deflection
	7.85		17.75	
	7.80		17.85	
	7.85		17.75	
Mean	7.83	Mean	17.78	9.95
Feb. 20th.			16.30	
	6.70		16.70	
	6.75		16.30	
	6.65		16.35	
Mean	6.70	Mean	16.42	9.68
Feb. 23rd.			16.70	
	6.80		16.55	
	6.85		16.65	
	6.70		16.55	
Mean	6.78	Mean	16.61	9.83

Mean of all observations Deflection 10.04

Depression 10.04 x 0.00583 = .0585 mm. T = $20^{\circ}.00+$

Experiment 3, 0.3 molar Mannite.

Solution was introduced Dec. 30, 1914, and exhausted twenty one times. Final readings were taken as follows:-

		Zero		Reading	Deflection
Jan. 12th.		10.00		25.40	
		10.00		25.30	
	Mean	10.00	Mean	25.35	15.35
Jan. 13th.		10.90		26.10	
		11.10		26.50	
		11.00		26.80	
	Mean	11.00	Mean	26.50	15.50
Jan. 14th.				24.95	
		9.80		24.90	
		9.75		25.10	
		9.70		25.10	
	Mean	9.75	Mean	25.00	15.25
		9.20		24.50	
		9.25		24.40	
		9.30		24.30	
	Mean	9.25	Mean	24.35	15.10
Jan. 16th.				25.10	
		9.75		25.05	
		9.85		25.10	
		9.80		25.10	
	Mean	9.80	Mean	25.09	15.29

0.3 molar Mannite (continued)

Jan. 17th,	Zero		Reading	Deflection
			24.70	
	9.00		24.55	
	8.95		24.65	
	9.05		24.70	
Mean	9.00	Mean	24.65	15.65
Jan. 18th.	8.70		24.20	
	8.60		24.35	
	8.80		24.30	
Mean	8.70	Mean	24.22	15.52
Jan. 20th.	8.40		24.05	
	8.00		23.75	
	8.20		23.70	
	8.30		23.95	
Mean	8.18	Mean	23.80	15.62
	9.10		24.30	
	9.10		24.20	
	9.05		24.25	
Mean	9.08	Mean	24.25	15.17
			24.10	
	8.90		24.05	
	8.85		23.90	
	9.00		24.05	
Mean	8.92	Mean	24.02	15.10

0.3 molar Mannite (continued)

Jan. 30th.	Zero		Reading	Deflection
	8.05		23.65	
	8.20		23.70	
	8.10		23.65	
	Mean 8.13	Mean	23.68	15.57
Jan. 31st.	8.80			
	8.70			
	8.60		23.85	
	8.65		23.75	
	8.70		23.85	
	Mean 8.70	Mean	23.82	15.13
	8.00			
	8.20		23.75	
	8.00		23.60	
	8.20		23.55	
	8.10		23.80	
	Mean 8.10	Mean	23.68	15.58
Jan. 32nd.	8.75			
	8.70		24.35	
	8.95		24.30	
	8.75		24.20	
	8.80		24.35	
	Mean 8.80	Mean	24.35	15.15

0.3 molar Mannite (continued)

Jan. 22nd.	Zero		Reading	Deflection
			23.75	
			23.70	
			23.70	
		Mean	23.72	15.62
Jan. 23rd.	8.15			
	8.10			
	8.15			
	Mean 8.13			
	8.30			
	8.15			
	8.30			
	Mean 8.18			
			23.80	
	8.30		23.95	
	8.20		23.95	
	8.85		23.90	
	Mean 8.22	Mean	23.90	15.72
Jan. 25th.	9.10		24.90	
	9.00		25.00	
	9.15		25.00	
	Mean 9.08	Mean	24.97	15.89

0.3 molar Mannite (continued)

		Zero		Reading	Deflection
Jan. 26th,		9.00		24.90	
		9.00		25.00	
		9.00		25.00	
	Mean	9.00	Mean	24.97	15.97
		9.10		25.00	
		9.30		25.05	
		9.20		25.10	
	Mean	9.17	Mean	25.05	15.88
Jan. 27th.		8.95		24.90	
		9.00		24.90	
		9.10		25.00	
	Mean	9.02	Mean	24.93	15.91

Mean of all observations Deflection 15.50

Depression 15.50 x 0.00583 = .0904 mm. T = 20°.00+

Experiment 4, 0.4 M. Mannite.

The solution was introduced Nov. 15,1914. and exhausted fifteen times

Final readings were taken as follow:-

	Zero	Readings	Deflection.
Dec. 2nd, 1914.	6.00		
	5.90	25.70	
	5.90	25.60	
	6.00	25.60	
Mean	5.95	Mean 25.63	19.68
		25.80	
	5.90	25.50	
	6.00	25.70	
	6.00	25.70	
Mean	5.97	Mean 25.68	19.71
Dec. 3rd.	5.00	25.00	
	4.90	25.90	
	5.00	25.00	
	5.00	25.00	
Mean	4.98	Mean 24.98	20.00
Dec. 4th.		26.30	
	6.20	26.35	
	6.35	26.10	
	6.30	26.30	
Mean	6.32	Mean 26.35	20.03

0.4 M. Mannite (continued)

Dec. 6th.	Zero	Reading	Deflection
	6.40	26.30	
	6.30	26.00	
	6.50	26.10	
Mean	6.40	Mean 26.10	19.70
	6.60	27.00	
	6.70	26.90	
Mean	6.65	Mean 26.95	20.30
Dec. 7th.		27.20	
		27.00	
	6.60	27.20	
	6.60	27.30	
	6.60	27.30	
Mean	6.60	Mean 27.20	20.60
		27.10	
	7.00	27.30	
	7.05	27.20	
	7.00	27.30	
Mean	7.02	Mean 27.32	20.20
Dec. 8th.	8.00	28.30	
	8,00	28,25	
	8.10	28.30	
Mean	8.03	Mean 28,27	20.24
	7.90	28.10	
	7.90	28.20	
	8.00	28.15	
Mean	7.93	Mean 28.15	20.22

0.4 M. Mannite (continued)

	Zero	Reading	Deflection
Dec. 9th.	8.00	28.50	
	8.05	28.60	
	8.00	28.70	
	8.00	28.50	
Mean	8.01	Mean 28.58	20.57
	7.80		
	8.10	28.30	
	7.80	28.10	
	8.00	28.30	
	7.80	28.10	
Mean	7.90	Mean 28.30	20.30
Dec.10th.	7.90	28.40	
	7.90	28.20	
	7.90	28.25	
Mean	7.90	Mean 28,28	20.38
	7.60	28.10	
	7.60	28.00	
	7.60	27.80	
Mean	7.60	Mean 27.97	20.37
	7.70	27.95	
	7.60	28.00	
	7.80	28,00	
Mean	7.70	Mean 27.98	20.28

0.4 M. Mannite (continued)

Dec. 10th.	Zero		Reading	Deflection
	8.10		28.50	
	8.00		28.35	
	8.10		28.50	
Mean	8.07	Mean	28,45	20.38
Dec. 11th.	8.10		28.70	
	8.10		28.70	
	8.30		28.80	
Mean	8.13	Mean	28.73	20.60
Dec. 14th.	8.80		28.80	
	8.80		29.00	
	8.70		29.00	
Mean	8.77	Mean	28.93	20,16
	8.20			
	8.10		28.30	
	8,20		28.40	
Mean	8.17	Mean	28.35	20.18
Dec. 16th.	8.80			
	8.80			
	8.80		29.30	
	8.80		29.40	
	8.90		29.40	
Mean	8.80	Mean	29.37	20.57

Mean of observations Deflection 20.32

Depression 20.32 x 0.00583 = .1184 mm. T = 20.00°+

Experiment 5, 0.5 molar Mannite.

The solution was introduced Oct. 22. 1914, and exhausted twelve times.

Final readings were taken as follows:-

	Zero		Readings	Deflection
Nov. 9th.	194.10		220.10	
	194.10		220.30	
	194.00		220.00	
	194.05		219.70	
Mean	194.05	Mean	220.02	25.97
Nov. 10th.	194.00		219.80	
	194.20		219.80	
	194.20		219.90	
	194.30		219.90	
	194.10		219.90	
Mean	194.16	Mean	219.86	25.70
Nov. 11th.			220.70	
			220.90	
			220.90	
	194.80		220.90	
	194.70		221.00	
	194.70		221.00	
Mean	194.73	Mean	220.90	26.17
Nov. 15th.			221.90	
			221.70	
	195.00		221.60	
	195.10		221.60	
	195.10		221.60	
	195.20		221.60	
Mean	195.10	Mean	221.63	26.53

0.5 molar Mannite (continued)

Nov. 16th.	Zero		Reading	Deflection
	195.80		221.90	
	195.80		221.90	
	196.00		221.90	
Mean	195.86	Mean	221.90	26.04
Nov. 17th.	194.30		220.80	
	194.40		320.90	
	194.30		220.90	
Mean	194.33	Mean	220.86	26.53
	194.70		221.00	
	194.70		221.00	
	194.60		221.00	
Mean	194.66	Mean	221.00	26.34
	194.60			
	194.50		221.00	
	194.80		221.00	
	194.60		221.00	
Mean	194.62	Mean	221.00	26.38
Nov. 19th.			232.70	
	196.10		232.80	
	196.20		232.70	
	196.30		232.60	
Mean	196.20	Mean	232.70	26.50

0.5 molar Mannite (continued)

Nov. 21st.	Zero		Reading	Deflection
	195.80		222.30	
	195.90		222.10	
	195.80		222.10	
	195.80		222.20	
	195.90		222.20	
	Mean 195.84	Mean	222.18	26.34
			222.50	
	196.10		222.70	
	196.00		222.70	
	196.10		222.70	
	Mean 196.05	Mean	222.65	26.60

Nov. 22nd. Change in zero due to substitution of paper scale for brass scale.

Nov. 23rd.	Zero		Reading	Deflection
	3.75			
	3.70			
	3.80			
	Mean 3.75			
	4.00		30.10	
	3.80		30.10	
	3.90		30.10	
	Mean 3.90	Mean	30.10	26.37
	4.20			
	4.20			
	4.10			
	4.20			
	Mean 4.17			

0.5 molar Mannite (continued)

Nov. 23rd.	Zero		Reading	Deflection
			30.40	
	4.30		30.30	
	4.20		30.30	
	4.20		30.40	
Mean	4.23	Mean	30.35	26.15
Nov.	4.30		30.60	
	4.30		30.50	
	4.20		30.40	
	4.30		30.60	
Mean	4.25	Mean	30.52	26.37
	4.30		30.65	
	4.30		30.60	
	4.30		30.65	
	4.30		30.60	
Mean	4.38	Mean	30.63	26.32
	3.80		30.20	
	3.90		30.20	
	4.00		30.10	
	4.00			
Mean	3.93	Mean	30.17	26.34

0.5 molar Mannite (continued)

Nov. 24th.	Zero		Reading	Deflection
	4.20		30.60	
	4.30		30.50	
	4.30		30.75	
	4.30		30.60	
Mean	4.30	Mean	30.61	26.31
	5.50		31.70	
	5.50		31.70	
	5.50		31.80	
Mean	5.50	Mean	31.73	26.23

Mean of all observations Deflection 26.28

Depression 26.28 x 0.00583 = .1532 mm. T = 20.00°

Tabulation of Results.

Normality.	Deflection	Depression
0.1-molar Mannite	4.90	.029 mm.
0.2 " "	10.04	.059 "
0.3 " "	15.30	.090 "
0.4 " "	20.32	.118 "
0.5 " "	26.28	.153 "

During the year 1913-1914, results were obtained by Frazer and Lovelace, working in collaboration with Mr. E. Miller, as follows:

	Depression
0.3-molar Mannite	.091 mm.
0.4 " "	.122 "
0.5 " "	.156 "

The theoretical lowerings, calculated from the formula of Raoult, are as follows. His equation is,

$$f - f' = f \times \frac{n}{N - n}$$

where,

f= 17.539 mm.[1] (at 20°)

f'= Vapor pressure of solution

N= gram molecules of solvent

n = gram molecules of solute.

	Depression
0.1-molar Mannite	0.031 mm.
0.2- " "	0.063 "
0.3 " "	0.094 "
0.4 " "	0.1245 "
0.5 "	0.1554 "

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1 Scheel & House, Ann. der Phys.4, 31, 715 (1910)

It is to be noted, that, since the absolute error is constant, the percentage error is necessarily less in the case of the higher concentrations.

If we calculate the osmotic pressure from the experimental values given in the first table, using the equation of Nernst[1]

$$P = \frac{p - p'}{p'} \times \frac{0.0821\ T \cdot 1000\ S}{M_o} \text{ atmospheres}$$

where P is the osmotic pressure, p the vapor pressure of water at the absolute temperature T, S the density of the solution, and M_o the molecular weight of the solvent and p' the vapor pressure of the solution, we obtain the following values:

Calculated osmotic pressure(in atmospheres) 0.5-m. Mannite 12.20

" " " " " 0.2-m. Mannite 4.60

Using the more exact equation of Nernst,[2]

$$P = \frac{0.0821\ T\ 1000\ S}{M_o} \ln \frac{p}{p'} \text{ atmospheres}$$

where the symbols have the same significance as above, we get,

Calculated osmotic pressure, 0.5-molar Mannite 12.14

" " " 0.2 " " 4.58

The experimentally determined values, taken from the work of Morse and Frazer[3], are as follows:

0.5-molar Mannite 11.96

0.2 " " 4.78

The results given in the first table are plotted in the following curve.

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1) Theoretical Chemistry, tr.by Tizard, Page 134.

2) " " " " 135.

3) The Osmotic Pressure of aqueous solutions (Carnegie Institution.

0.1 molar Mannite

Values Plotted. { .0290, .0295, 0.300, 0.295, 0.306 } Ordinate = .0025 m.m. Abscissa = .002 N.

CURVE SHOWING MOLECULAR LOWERING.

Summary

In the brief historical survey, the evolution of both static and dynamic methods was traced. It was shown that the static method, owing to supposedly unavoidable constant sources of error, was superceded by the dynamic method; but that the latter, although an improvement over the old form of the static method,still leaves much to be desired. The great laws governing the vapor pressure of solutions were discovered , however, by means of the static method, (e.g. the laws of von Babo, Wüllner, and Raoult); while the results of more recent investigations with the dynamic method, have been used to measure dissociation, and to furnish evidence concerning hydration in solution.

The improved form of the static method as evolved by Frazer and Lovelace was then described, and the great increase in accuracy over all former methods shown to be due to the elimination of the four great sources of error supposedly inherent in the static method. As the result of investigations with this apparatus, we may draw the following conclusions concerning the accuracy of the method and the sources of error.

1.The limit of accuracy of the method is 0.00058 mm.

2.Air in amounts greater than 0.0004 mm. was proved to be absent before taking final readings. This was done by means of the McLeod gauge. It was further found that the last traces of air was much more easily removed from concentrated than from dilute solutions.

3. Surface concentration was avoided by automatic stirring.

4. The temperature was regulated to 0.001°. Variations of more than 0.002°, were shown to affect the readings.

It is believed that the values given for the vapor pressure lowerings of aqueous solutions of mannite in the first table, are correct to within 0.001 mm. While the results obtained last year with a different form of the same apparatus are higher than the results given, it is to be pointed out that the method of stirring has been much improved since the first results were obtained, and that the bath regulation is much better. The fact that the values are uniformly lower than the theoretical lowerings deduced from the equation of Raoult is no proof of their incorrectness, as the formula of Raoult is known to hold only for very dilute solutions of non-electrolytes, and was evolved primarily not for aqueous solutions, but for organic solvents. The comparatively close agreement, (within 2 %) of the calculated osmotic pressures (based on the vapor pressure values) with the carefully determined experimental values of Morse and Frazer, is believed to be further proof of the accuracy of the results. This conclusion is brought out by the curve showing the molecular lowering, which is practically a straight line.

BIOGRAPHICAL SKETCH.

The author of this dissertation was born in Baltimore, Maryland, July 15, 1888. He received his early education in the public schools of Baltimore, graduating in 1907 from the Baltimore City College. During the year 1907-1908, he was assistant chemist at the Baltimore Copper Smelting and Rolling Co., leaving to enter the Johns Hopkins University in 1908, where he completed the chemical-geological course in 1911. From June 1911, to October, 1912, he was assistant chemist, Test Bureau, B.&O.R.R. Co., at Baltimore, Md. In 1912, he reentered the Johns Hopkins University, where for the past three years he has pursued graduate courses in Chemistry, Physical Chemistry, and Geology. During the last two years of residence, he has held University scholarships.